PCT WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : C07D 311/92, 311/78, 409/04, G02B 5/23 — A1

(11) International Publication Number: **WO 98/42695**

(43) International Publication Date: 1 October 1998 (01.10.98)

(21) International Application Number: PCT/GB98/00905

(22) International Filing Date: 25 March 1998 (25.03.98)

(30) Priority Data:
9706203.8 25 March 1997 (25.03.97) GB

(71) Applicant (*for all designated States except US*): JAMES ROBINSON LIMITED [GB/GB]; Hillhouse Lane, P.O. Box 23, Huddersfield HD1 6BU (GB).

(72) Inventors; and

(75) Inventors/Applicants (*for US only*): CLARKE, David, Allan [GB/GB]; 23 Wentworth Court, Rastrick, Brighouse HD6 3XD (GB). HERON, Bernard, Mark [GB/GB]; 63 Welton Road, Brough, East Riding, Yorkshire HU15 1AB (GB). GABBUTT, Christopher, David [GB/GB]; 7 New Row, Knowle Green, Preston, Lancashire PR3 2YS (GB). HEPWORTH, John, David [GB/GB]; 2 Carnoustie Close, Fulwood, Preston, Lancashire PR2 7ER (GB). PARTINGTON, Steven, Michael [GB/GB]; 48 Woodroyd, Golcar, Huddersfield HD7 4PG (GB). CORNS, Stephen, Nigel [GB/GB]; 10 Beech Street, Paddock, Huddersfield HD1 4JN (GB).

(74) Agents: WAIN, Christopher, Paul et al.; A.A. Thornton & Co., Northumberland House, 303–306 High Holborn, London WC1V 7LE (GB).

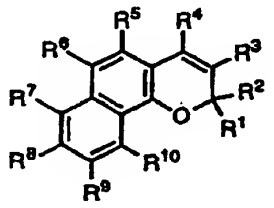
(81) Designated States: GB, JP, US, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published

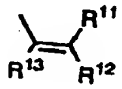
With international search report.

Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

(54) Title: INTENSE COLOURING PHOTOCHROMIC 2*H*–NAPHTHO[1,2–*b*]PYRANS AND HETEROCYCLIC PYRANS



(I)



(II)

(57) Abstract

A naphtho [1,2–*b*] pyran of general formula (I), wherein one or both of R^1 and R^2 is a 4–aminoaryl group; R^5 is selected from linear or branched C_1–C_{10} alkyl, C_1–C_{20} cycloalkyl, C_1–C_{20} bicycloalkyl, C_1–C_{20} polycycloalkyl, linear or branched C_1–C_{10} haloalkyl, linear or branched C_1–C_{10} perhaloalkyl, linear or branched C_1–C_{10} perhaloalkenyl, linear or branched C_1–C_{10} alkenyl, C_1–C_{10} alkynyl, linear or branched C_1–C_{10} alkoxy, linear or branched C_1–C_{10} alkylthio, linear or branched C_1–C_{10} alkoxy (linear or branched C_1–C_{10} alkyl), linear or branched C_1–C_{10} hydroxyalkyl, linear or branched C_1–C_{10} aminoalkyl, aryl, phenyl, heteroaryl, halogen, nitrile, nitro, amino, linear or branched C_1–C_{20} alkoxycarbonyl, hydroxyl, formyl, acetyl, amido, C_1–C_5 alkylamido, C_1–C_5 dialkylamido, aroyl, benzoyl, alkyl C_1–C_5 amino, dialkyl C_1–C_5 amino, arylamino, diarylamino, aryl C_1–C_5 alkylamino and cyclicamino groups; arylsulfinyl, arylsulfanyl, arylsulfonyl, linear or branched C_1–C_{10} alkylsulfonyl, $P(O)(O–C_1–C_{10}$ alkyl$)_2$ or is the alkenyl function (II), wherein R^{11} and/or R^{12} and/or R^{13} is hydrogen or is as defined for R^5, and R^3, R^4 and R^6–R^{10} are each hydrogen or as defined R^1, R^2 or R^5. The compounds may be combined with a polymeric host material such as a plastic or a glass to make a sunglass lens, an ophthalmic lens or a window.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

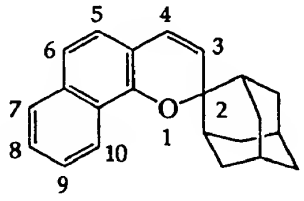
AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece			TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	NZ	New Zealand		
CM	Cameroon			PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

Intense Colouring Photochromic 2H-Naphtho[1,2-b]pyrans and Heterocyclic Pyrans

The present invention relates to certain new photochromic pyran derivatives and to their use.

Photochromism is a well-known physical phenomenon which is observed with certain classes of chemical compounds. A detailed discussion of this phenomenon can be found in "Photochromism: Molecules and Systems," Studies in Organic Chemistry 40, Eds. H Dürr and H. Bouas-Laurent, Elsevier, 1990.

The 2*H*-naphtho[1,2-*b*]pyran system is known to be capable of exerting a photochromic effect as described, for example, U. S. Patent No. 3,567,605 and U. S. Patent No. 4,826,977. U. S. Patent No. 3,567,605 provides an example of a 2*H*-naphtho[1,2-*b*]pyran which remains coloured at ambient temperatures for several hours, and U. S. Patent No. 4,826,977 describes a series of yellow/orange colouring 2*H*-naphtho[1,2-*b*]pyrans containing a spiro-adamantane group at the 2-position, amongst other 2*H*-[1]benzopyran and isomeric naphthopyran systems. The basic structural unit of the 2*H*-naphtho[1,2-*b*]pyran system, in this instance substituted at C-2 with a spiro-adamantane group, is illustrated below.



A range of purple/blue colouring 2(4-aminophenyl)-2-alkyl-2*H*-naphtho[1,2-*b*]pyrans have been described in U. S. Patent No. 4,818,096 and European Patent No. 0,250,193 describes a range of photochromic naphtho-[1,2-*b*] and [2,1-*b*]pyrans which bear one or two aminophenyl substituents on the carbon atom adjacent to the oxygen heteroatom. In this patent it is stated that substitution in the ring positions, sites 5 - 10, other than at site 6 has little influence on the photochromic behaviour of the compounds.

A series of photochromic 2*H*-naphtho[1,2-*b*]pyrans, amongst other 2*H*-[1]benzopyrans and isomeric naphthopyrans, bearing a cyclopropyl group as one of the substituents at the 2-position is described in article WO92/01959. It is also commented that the compound 2-cyclopropyl-2-*p*-methoxyphenyl-5-methyl-2*H*-naphtho[1,2-*b*]pyran and several other

analogues are of particular current interest, but no reasons were presented either to substantiate such interest or as to any significance of the 5-methyl group.

It is stated in U. S. Patent No. 5,066,818 (1991) that "The compound, 2,2-diphenyl-2*H*-naphtho[1,2-*b*]pyran, also colours on exposure to near ultraviolet light at room temperature but does not bleach in a reasonable period of time. Substitution of the phenyl substituents in the *meta* and *para* positions have little effect on the rate of bleaching of these compounds."

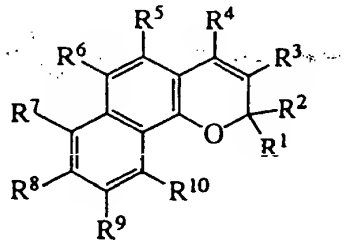
The very high optical density of 2,2-diaryl-2*H*-naphtho[1,2-*b*]pyrans achieved under irradiation and their slow attendant fade (bleaching) on removal of the source of irradiation relative to the photochromic properties displayed by the isomeric 3,3-diaryl-3*H*-naphtho[2,1-*b*]pyrans has been recently noted by B. van Gemert *et al.* (*Mol. Cryst. Liq. Cryst.*, 1994, 246, 67). The relatively slow attendant fade of the 2,2-diaryl-2*H*-naphtho[1,2-*b*]pyrans was rationalised by the absence of steric crowding in the ring opened (coloured) quinoidal/zwitterionic forms. Such steric crowding is thought to be present for the ring opened form of the 3,3-diaryl-3*H*-naphtho[2,1-*b*]pyrans and accounts for their relatively rapid fade.

Pilkington Brothers Limited have also commented on the fading of photochromic materials in Research Disclosure. Two structurally similar deep colouring photochromic 2,2-diaryl-2*H*-naphtho[1,2-*b*]pyrans, namely 2,2-bis(4-methoxyphenyl)-5,6-dimethyl-2*H*-naphtho[1,2-*b*]pyran and 2-(4-methoxyphenyl)-2-(4-trifluoromethylphenyl)-5,6-dimethyl-2*H*-naphtho-[1,2-*b*]pyran are described, which exhibit markedly improved attendant fade compared with the non-methyl substituted analogues. These improved rates of fade are attributed to the combined presence of methyl groups at the 5- and 6-positions, which are said to exert steric pressures upon the ring opened (coloured) quinoidal/zwitterionic forms, thereby enhancing the ring closure to the uncoloured naphthopyran system. However, these fast fade materials described by Pilkington plc with substituents at both the 5- and 6- positions are difficult to make, requiring a long multi-stage process which renders them unattractive commercially. Thus the use of two substituents at the 5- and 6-positions to achieve rapid fade in these 2,2-diaryl compounds has the disadvantage of manufacture complexities.

Two recent U. S. Patents, 5,458,814 and 5,514,817 describe the synthesis of a range fast fading intensly colouring 5-substituted or 5,6-disubstituted 2,2-diaryl-2*H*-naphtho[1,2-*b*]pyrans and phenanthropyrans.

We have investigated these known photochromic compounds and have found that, for enhanced intense colour generation, compounds having 2-(aminoaryl)-2-aryl or 2,2-bis(aminoaryl) substituents are preferred. Also the presence of a 5-substituent in these 2,2-diaryl-2*H*-naphtho[1,2-*b*]pyrans ensures rapid fading of the red or orange colour generated upon irradiation.

According to the present invention, there is provided a photochromic compound of the formula I



I

In graphic formula I above, R^1 and R^2 are each selected from unsubstituted, mono-, di- or polysubstituted aryl groups, phenyl and naphthyl, preferably mono- or di-substituted phenyl or naphthyl. Additionally R^1 and or R^2 may be selected from the following heteroaryl groups, thienyl, benzo[*b*]thienyl, furyl, benzo[*b*]furyl, pyrryl, indolyl.

The substituents for the aryl and heteroaryl groups representing R^1 and R^2 may be amino, alkyl C_1 - C_5 amino, dialkyl C_1 - C_5 amino, arylamino, arylalkyl C_1 - C_5 amino, diarylamino and cyclic amino groups (for example, aziridino, pyrrolidino, piperidino, morpholino, thiomorpholino, indolino, piperazino, C_1 - C_5 *N*-alkyl-piperazino). Other substituents in addition to the specified amino function may include, in any remaining positions, hydrogen, C_1 - C_5 alkyl, C_1 - C_5 haloalkyl, C_1 - C_5 alkoxy, C_1 - C_5 alkoxy(C_1 - C_5)alkyl, amino-C_1 - C_5 alkyl, hydroxy-C_1 - C_5 alkyl, halogen.

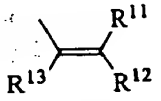
Phenyl, aryl and heteroaryl ring substituents may be located at the *o*-, *m*- or *p*-positions. Typically each phenyl group contains less than 3 substituents.

R^3 and R^4 are hydrogen.

R^5 may be selected from C_1 - C_{10} alkyl, C_1 - C_{10} haloalkyl, C_1 - C_{10} perfluoroalkyl, C_1 - C_5 perfluoroalkenyl, C_1 - C_5 alkenyl, C_1 - C_5 alkynyl, C_1 - C_{10} alkoxy, C_1 - C_{10} perfluoroalkoxy, C_1 - C_5 alkoxy(C_1 - C_5) alkyl, C_1 - C_5 hydroxyalkyl, halogen, nitrile, nitro, amino, C_1 - C_5 alkylamino, C_1 - C_5 dialkylamino, cyclic amino (for example, aziridino, pyrrolidino, piperidino,

morpholino, thiomorpholino, indolino, piperazino, C_1 - C_5 *N* - alkylpiperazino), arylamino, diarylamino, aryl C_1 - C_5 alkylamino, C_1 - C_5 oxoalkyl, phenyl, aryl, substituted aryl, naphthyl, substituted naphthyl, aroyl, substituted aroyl, formyl, carboxyl, C_1 - C_{20} alkoxycarbonyl, C_1 - C_5 haloalkyloxycarbonyl, aryloxylcarbonyl, substituted aryloxylcarbonyl.

R^5 may also be selected from the alkenyl function illustrated immediately below:

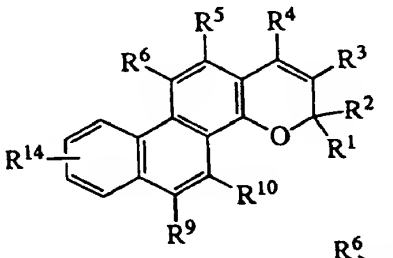


Where R^{11} and or R^{12} and or R^{13} will be selected from those substituents specified for R^1 and R^2 in formula I. In addition to these substituents R^{11} and R^{12} and R^{13} may be selected from CN, NO_2, CHO, C_1 -C_5 alkoxycarbonyl, benzoyl, and phenylsulfonyl.

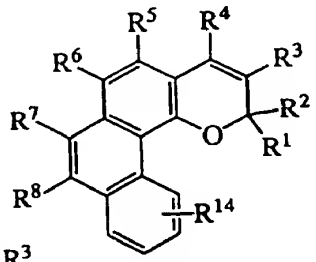
In graphic formula I R^6, R^7, R^8, R^9 and R^{10} may be selected from hydrogen, in addition to those groups specified for R^5 above.

Typically, though not always, two or three groups selected from R^7, R^8, R^9 and R^{10} are hydrogen.

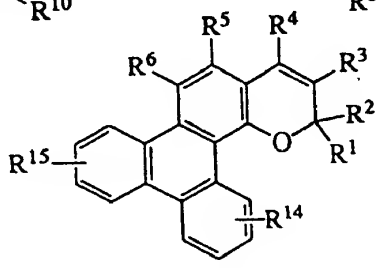
In addition to the 2*H*-naphtho[1,2-*b*]pyran compounds of formula I, the present invention includes the isomeric phenanthropyrans of the general formula II and III and benzo[*l*]phenanthropyrans of the general formula IV



II



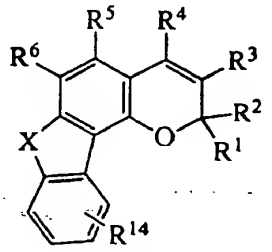
III



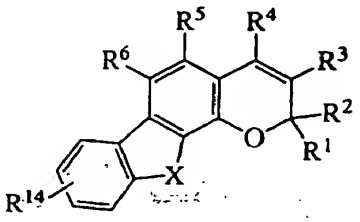
IV

In graphic formula II, III andIV R^1 to R^{13} are as specified for graphic formula I and R^{14} and R^{15} may be selected from those substituents specified for R^6.

In addition to the 2*H*-naphtho[1,2-*b*]pyran compounds of formula I, the present invention includes the isomeric heterocyclicpyrans of the general formula V and VI



V



VI

In graphic formula IV and V R^1 to R^{14} are as specified for graphic formula I and the heteroatom X may be selected from O, S, NH, and substitiued N for example C_1 - C_{10} alkyl, C_1 - C_{10} haloalkyl, C_1 - C_{10} perfluoroalkyl, benzyl, phenyl, tosyl, benzoyl, amino-C_1 - C_5 alkyl, hydroxy-C_1 - C_5 alkyl.

The photochromic properties exhibited by the novel pyran compounds of the present invention, namely those of high induced optical density and rapid bleaching of the red or orange coloured form, render these compounds particularly useful as photochromic materials for incorporation into polymeric host materials so as to impart photochromic properties to the said polymeric host materials. Examples of applications of the polymeric host materials containing photochromic materials of the present invention include the manufacture of lenses for sunglasses and ophthalmic lenses, optical filters and windows for vehicles such as cars (including sunroofs), aircraft and ships and architectural uses e.g. windows for homes and for photochromic 'stained glass' windows.

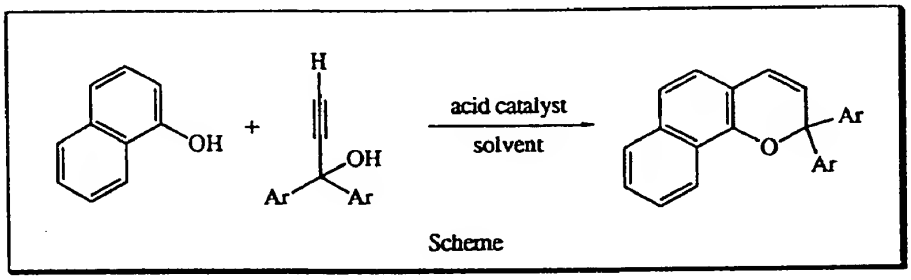
The photochromic pyrans of the present invention are incorporated into the 'plastic' host material by well established protocols for example as described in European Patent No. 0254020 or U. S. Patent No. 5,066,818.

The high induced optical density of the photochromic compounds of the present invention enables the amount of the photochromic material required so as to impart a useful degree of photochromism to a polymeric host material or to a solution to be greatly reduced, thereby enabling a considerable saving of synthetic effort and cost. Furthermore, the use of reduced quantities of the photochromic materials of the present invention has the bonus that there is a consequent reduction in any undesirable colour that

the photochromic materials may impart in the bleached state, either by way of inherent colour of the material itself or by the formation of coloured fatigue / degradation products through use of the photochromic material.

Typical host materials are optically clear polymer materials, such as polymers of polyol (allyl carbonate) - monomers, polyacrylates such as polymethylmethacrylates, cellulose acetate, cellulose triacetate, cellulose acetate propionate, cellulose acetate butyrate, poly(vinyl acetate), poly(vinyl alcohol), polyurethanes, polycarbonate, polyethylene terephthalate, polystyrene, poly(triethyleneglycol dimethylacrylate), poly(diethyleneglycol bis(allyl carbonate)) and various copolymer mixes.

The pyran compounds of the present invention may be prepared by a general method which is based on the following reaction scheme:



Scheme

This general synthetic methodology has been descibed in detail, for example, by L. Merlini in 'Advances in Heterocyclic Chemistry,' 1975, vol. 18, page 159, and by R. Guglielmetti in "Photochromism: Molecules and Systems," Studies in Organic Chemistry 40, chp. 8, Eds. H Dürr and H. Bouas-Laurent, Elsevier, 1990, and also in several patent documents, for example, U. S. Patent No. 5,066,818; U. S. Patent No. 4,990,287, WO 92/09593 and WO95/05382. The synthesis of the propargyl alcohols shown in the scheme above are obtained in a known manner, for example, T. F. Rutledge in 'Acetylenic Compounds,' Reinhold, New York, 1968. The 1-naphthols and related hydroxy compounds are either commercially available or obtained by known synthetic methods, or derived from such methods. Some of the 1-naphthols and related hydroxy compounds or precursors thereof have been described in the chemical literature, for example, ethyl 1-acetoxydibenzo thiophene-3-carboxylate see (S. Gronowitz *et al.*, Acta. Pharm. Suec., 1978, 15, 337) and 3-hydroxypropyl-1-naphthol see (R. F. Frank *et al.*, J. Chem. Soc., Chem. Commun., 1984, 761). The use of the Stobbe condensation to prepare 1-naphthols has also been discussed (see Organic Reactions 1951, 6, 1).

The acid catalyst may be selected from acidic alumina (Brockmann 1), acetic acid, trifluoroacetic acid, silica, clays (e.g. montmorillionite, tonsil) or acidic exchange resins.

Organic solvents frequently employed for the reaction include benzene, toluene, xylene and relatively high boiling alkanes.

The following examples illustrate but do not limit the invention:

Example 1: Methyl 9-methoxy-2-phenyl-2-(2-thienyl)-2*H*-naphtho[1,2-*b*]pyran-5-carboxylate

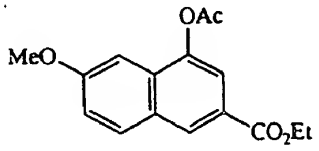
(a) Ethyl 4-acetoxy-6-methoxy-2-naphthoate

A solution of freshly distilled *p*-anisaldehyde (20g, 146.9 mmol) and diethyl succinate (38.4g, 220.3 mmol) in anhydrous ethanol (50 cm^3), was added dropwise over 45 minutes to a vigorously stirred warm ~ 40 - 50 °C, solution of sodium ethoxide (from sodium 6.75g, 293.8 mmol) in anhydrous ethanol (450 cm^3) under N_2. On completion of the addition the solution was refluxed for 4 hours and then cooled to room temperature.

The reaction mixture was reduced to ~ 1/5 of the original volume and the resulting viscous oil was diluted with water (700 cm^3), cautiously acidified with c. HCl and the resulting two phase mixture extracted with ethyl acetate (5 x 100 cm^3). The combined EtOAc solutions were extracted with aq. sat. $NaHCO_3$ solution (6 x 100 cm^3). The combined aq. $NaHCO_3$ solutions were cautiously acidified with c. HCl and the resulting two phase mixture extracted with EtOAc (4 x 100 cm^3). The combined EtOAc extracts were dried (Na_2SO_4) and evaporated to afford a yellow mobile oil.

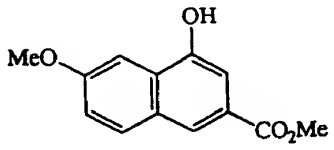
A solution of the aforegoing yellow oil and anhydrous sodium acetate (12.05g, 146.9 mmol) in acetic anhydride (180 cm^3) was refluxed for 3 hours. The solution was cooled to room temperature and then diluted with water (2000 cm^3) and allowed to stir for 1.5 hours. The resulting pale brown solid was collected by vacuum filtration, washed well with water (~500 cm^3) and air dried.

The solid was recrystallised from EtOAc / hexane and Norit (activated charcoal) to give ethyl 4-acetoxy-6-methoxy-2-naphthoate (yield = 21.2 g, theoretical yield = 42.35 g, 50 %, m. p. = 103.5 -104.5 °C (uncorrected)).



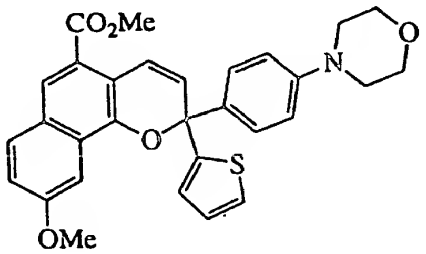
(b) Methyl 4-hydroxy-6-methoxy-2-naphthoate

A solution of ethyl 4-acetoxy-6-methoxy-2-naphthoate (3.0g, 10.4 mmol) and sodium hydroxide (2.5g, 62.5 mmol) in water (60 cm^3) and ethanol (15 cm^3) was maintained at 80 - 90 °C for 3 hours. The cooled solution was poured into water (400 cm^3) and cautiously acidified with c. HCl. The resulting suspension was extracted with EtOAc (5 x 75 cm^3). The combined extracts were dried (Na_2SO_4) and evaporated to give a pale brown solid. This solid was dissolved in methanol (50 cm^3) containing c. H_2SO_4 (~ 1 cm^3) and was refluxed for 4 hours. The cooled mixture was diluted with water (500 cm^3) and extracted with EtOAc (4 x 50 cm^3). The combined extracts were washed with aq. sat. $NaHCO_3$ (2 x 100 cm^3) and water (100 cm^3). Removal of the dried (Na_2SO_4) EtOAc gave a pale brown solid which was recrystallised from EtOAc/hexane to afford methyl 4-hydroxy-6-methoxy-2-naphthoate (yield = 1.63g, theoretical yield = 2.41g, 68%, m.p. = 193 - 195 °C (uncorrected)).

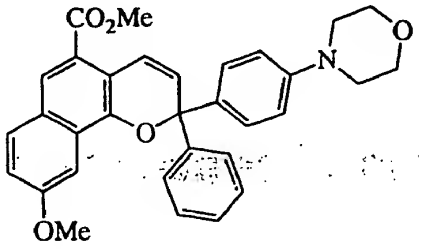


(c) Methyl 9-methoxy-2-phenyl-2-(2-thienyl)-2*H*-naphtho[1,2-*b*]pyran-5-carboxylate

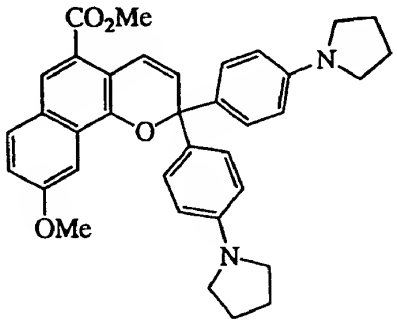
A solution of methyl 4-hydroxy-6-methoxy-2-naphthoate (0.45g, 1.8 mmol) and 1-(4-morpholinophenyl)-1-(2-thienyl)prop-2-yn-1-ol (0.55g, 1.8 mmol) in toluene (45 cm^3) containing acidic alumina (Brockmann 1), (4.0g) was refluxed for 60 minutes. The cooled solution was filtered and the alumina was washed well with EtOAc (200 cm^3). Removal of the solvent gave an oil which solidified on standing at RT. Recrystallisation twice from EtOAc/hexane gave methyl 9-methoxy-2-phenyl-2-(2-thienyl)-2*H*-naphtho[1,2-*b*]pyran-5-carboxylate (yield = 0.49 g, theoretical yield = 0.93g 52%, m.p. = 186 - 188°C (uncorrected)).



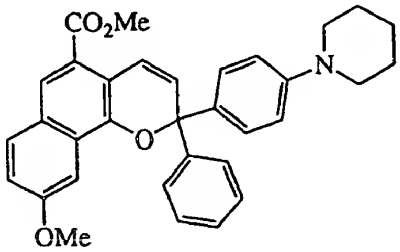
Example 2: Methyl 9-methoxy-2-(4-morpholinophenyl)-2-phenyl-2*H*-naphtho[1,2-*b*]pyran-5-carboxylate, m.p. = 175 - 177 °C (uncorrected). This compound was obtained by a similar protocol to example 1 above using the requisite starting materials.



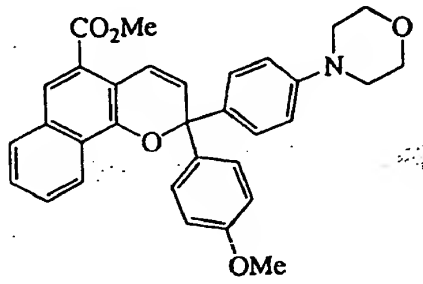
Example 3: Methyl 9-methoxy-2,2-bis(4-pyrrolidinophenyl)-2*H*-naphtho[1,2-*b*]pyran-5-carboxylate, m.p. = 210 - 215 °C (uncorrected). This compound was obtained by a similar protocol to example 1 above using the requisite starting materials.



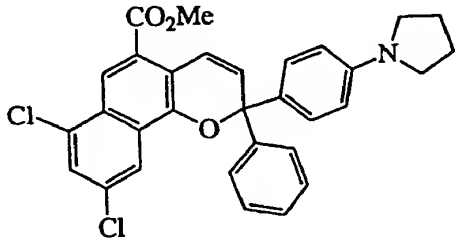
Example 4: Methyl 9-methoxy-2-phenyl-2-(4-piperidinophenyl)-2*H*-naphtho[1,2-*b*]pyran-5-carboxylate, m.p. = 164 - 167 °C (uncorrected). This compound was obtained by a similar protocol to example 1 above using the requisite starting materials.



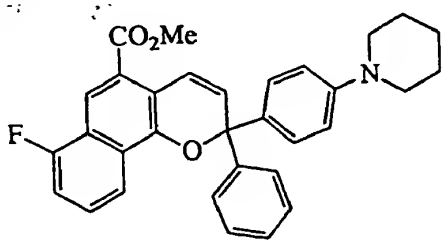
Example 5: Methyl 2-(4-methoxyphenyl)-2-(4-morpholinophenyl)-2*H*-naphtho[1,2-*b*]pyran-5-carboxylate, m.p. = 177 - 179 °C (uncorrected). This compound was obtained by a similar protocol to example 1 above using the requisite starting materials.



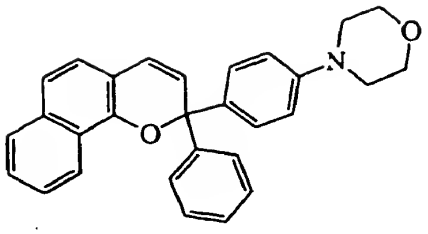
Example 6: Methyl 7,9-dichloro-2-(4-pyrrolidinophenyl)-2-phenyl-2*H*-naphtho[1,2-*b*]pyran-5-carboxylate, m.p. = 162 - 165 °C (uncorrected). This compound was obtained by a similar protocol to example 1 above using the requisite starting materials.



Example 7: Methyl 7-fluoro-2-(4-piperidinophenyl)-2-phenyl-2*H*-naphtho[1,2-naphtho[1,2-*b*]pyran-5-carboxylate, m.p. = 165 - 168 °C (uncorrected). This compound was obtained by a similar protocol to example 1 above using the requisite starting materials.



Comparative example 1: 2-(4-morpholinophenyl)-2-phenyl-2*H*-naphtho[1,2-*b*]pyran, m.p. = 131 - 134 °C (uncorrected).



Comparative example 2: Methyl 9-methoxy-2,2-bis(4-methoxyphenyl)-2*H*-naphtho[1,2-*b*]pyran-5-carboxylate

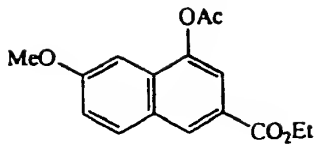
(a) Ethyl 4-acetoxy-6-methoxy-2-naphthoate

A solution of freshly distilled *p*-anisaldehyde (20g, 146.9 mmol) and diethyl succinate (38.4g, 220.3 mmol) in anhydrous ethanol (50 cm^3) was added dropwise over 45 minutes to a vigorously stirred warm ~ 40 - 50 °C, solution of sodium ethoxide (from sodium 6.75g, 293.8 mmol) in anhydrous ethanol (450 cm^3) under N_2. On completion of the addition the solution was refluxed for 4 hours and then cooled to room temperature.

The reaction mixture was reduced to ~ 1/5 of the original volume and the resulting viscous oil was diluted with water (700 cm^3), cautiously acidified with c. HCl and the resulting two phase mixture extracted with ethyl acetate (5 x 100 cm^3). The combined EtOAc solutions were extracted with aq. sat. $NaHCO_3$ solution (6 x 100 cm^3). The combined aq. $NaHCO_3$ solutions were cautiously acidified with c. HCl and the resulting two phase mixture extracted with EtOAc (4 x 100 cm^3). The combined EtOAc extracts were dried (Na_2SO_4) and evaporated to afford a yellow mobile oil.

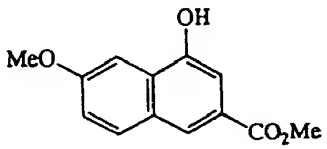
A solution of the aforegoing yellow oil and anhydrous sodium acetate (12.05g, 146.9 mmol) in acetic anhydride (180 cm^3) was refluxed for 3 hours. The solution was cooled to room temperature and then diluted with water (2000 cm^3) and allowed to stir for 1.5 hours. The resulting pale brown solid was collected by vacuum filtration, washed well with water (~500 cm^3) and air dried.

The solid was recrystallised from EtOAc / hexane and Norit (activated charcoal) to give ethyl 4-acetoxy-6-methoxy-2-naphthoate (yield = 21.2 g, theoretical yield = 42.35 g, 50 %, m. p. = 103.5 -104.5 °C (uncorrected)).



(b) Methyl 4-hydroxy-6-methoxy-2-naphthoate

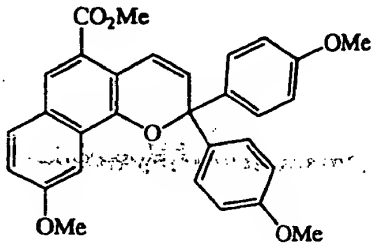
A solution of ethyl 4-acetoxy-6-methoxy-2-naphthoate (3.0g, 10.4 mmol) and sodium hydroxide (2.5g, 62.5 mmol) in water (60 cm^3) and ethanol (15 cm^3) was maintained at 80 - 90 °C for 3 hours. The cooled solution was poured into water (400 cm^3) and cautiously acidified with c. HCl. The resulting suspension was extracted with EtOAc (5 x 75 cm^3). The combined extracts were dried (Na_2SO_4) and evaporated to give a pale brown solid. This solid was dissolved in methanol (50 cm^3) containing c. H_2SO_4 (~ 1 cm^3) and was refluxed for 4 hours. The cooled mixture was diluted with water (500 cm^3) and extracted with EtOAc (4 x 50 cm^3). The combined extracts were washed with aq. sat. $NaHCO_3$ (2 x 100 cm^3) and water (100 cm^3). Removal of the dried (Na_2SO_4) EtOAc gave a pale brown solid which was recrystallised from EtOAc/hexane to afford methyl 4-hydroxy-6-methoxy-2-naphthoate (yield = 1.63g, theoretical yield = 2.41g, 68%, m.p. = 193 - 195 °C (uncorrected)).



(c) Methyl 9-methoxy-2,2-bis(4-methoxyphenyl)-2*H*-naphtho [1,2-*b*]pyran-5-carboxylate.

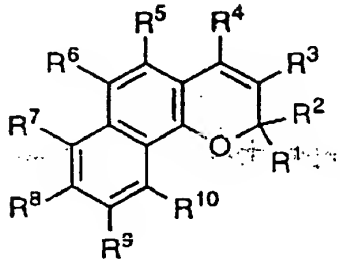
A solution of methyl 4-hydroxy-6-methoxy-2-naphthoate (1.0g, 4.3 mmol) and 1,1-di(4-methoxyphenyl)prop-2-yn-1-ol (1.16g, 4.3 mmol) in toluene (45 cm^3) containing acidic alumina (Brockmann 1), (4.0g) was refluxed for 45 minutes. The cooled solution was filtered and the alumina was washed well with EtOAc (200 cm^3). The organic filtrate was washed with aqueous sodium hydroxide (2M, 2 x 50 cm^3) and water (100 cm^3). Removal of the dried (Na_2SO_4) EtOAc gave an oil which was flash chromatographed over silica using 25% EtOAc in hexane as the eluent to afford a pale yellow solid. Recrystallisation from EtOAc/hexane gave methyl

9-methoxy-2,2-bis(4-methoxyphenyl)-2*H*-naphtho[1,2-*b*]pyran-5-carboxylate (yield = 0.79g, theoretical yield = 2.08g 38%, m.p. = 162.5 - 164.0 °C (uncorrected)).



CLAIMS:

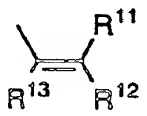
1. A naphtho[1,2-*b*]pyran of general formula (I)



(I)

wherein one or both of R^1 and R^2 is a 4-aminoaryl group;

R^5 is selected from linear or branched C_1-C_{10} alkyl, C_1-C_{20} cycloalkyl, C_1-C_{20} bicycloalkyl, C_1-C_{20} polycycloalkyl, linear or branched C_1-C_{10} haloalkyl, linear or branched C_1-C_{10} perhaloalkyl, linear or branched C_1-C_{10} perhaloalkenyl, linear or branched C_1-C_{10} alkenyl, C_1-C_{10} alkynyl, linear or branched C_1-C_{10} alkoxy, linear or branched C_1-C_{10} alkylthio, linear or branched C_1-C_{10} alkoxy (linear or branched C_1-C_{10} alkyl), linear or branched C_1-C_{10} hydroxyalkyl, linear or branched C_1-C_{10} aminoalkyl, aryl, phenyl, heteroaryl, halogen, nitrile, nitro, amino, linear or branched C_1-C_{20} alkoxycarbonyl, hydroxyl, formyl, acetyl, amido, C_1-C_5 alkyl amido, C_1-C_5 dialkylamido, aroyl, benzoyl, alkyl C_1-C_5 amino, dialkyl C_1-C_5 amino, arylamino, diarylamino, aryl C_1-C_5 alkylamino and cyclicamino groups; arylsulfinyl, arylsulfanyl, arylsulfonyl, linear or branched C_1-C_{10} alkylsulfonyl, $P(O)(O\text{-}C_1\text{-}C_{10}\ \text{alkyl})_2$ or is the alkenyl function:



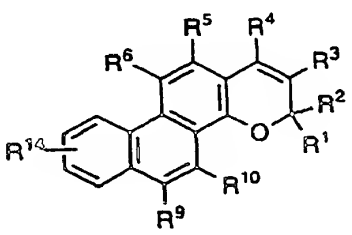
wherein R^{11} and/or R^{12} and/or R^{13} is hydrogen or is as defined for R^5 and R^3, R^4 and R^6 - R^{10} are each hydrogen or as defined for R^1, R^2 or R^5.

2. A naphtho[1,2-*b*]pyran according to claim 1, wherein the amino group alkyl is C_1-C_5 amino, dialkyl C_1-C_5 amino, arylamino, diarylamino, aryl C_1-C_5 alkylamino or a cyclicamino group.

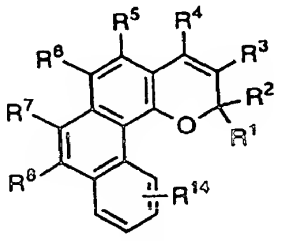
3. A naphtho[1,2-*b*]pyran according to claim 1 or 2, wherein the 4-aminoaryl group is further substituted in addition to the specified amino function and in any remaining positions, with hydrogen, C_1-C_5 alkyl, C_1-C_5 haloalkyl, C_1-C_5 perhaloalkyl, C_1-C_5 alkoxy, C_1-C_5 alkylthio, C_1-C_5 hydroxyalkyl, C_1-C_5 alkoxy, C_1-C_5 alkyl, C_1-C_5 aminoalkyl, halogen, C_1-C_5 alkoxycarbonyl, formyl, nitrile, carboxyl, acetyl, amino, alkyl C_1-C_5 amino, dialkyl C_1-C_5 amino, arylamino, diarylamino, aryl C_1-C_5 alkylamino or a cyclicamino group.

4. A naphtho[1,2-*b*]pyran according to claim 1, 2 or 3, wherein the cyclicamino group is aziridino, pyrrolidino, piperidino, morpholino, thiomorpholino, indolino, piperazino, C_1-C_5 *N*-Alkylpiperazino or *N*-arylpiperazino.

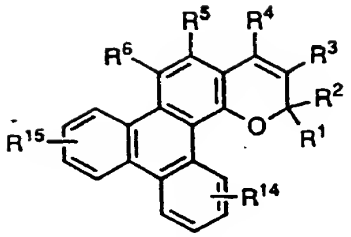
5. A naphtho[1,2-*b*]pyran according to any of claims 1, 2, 3 or 4 of the general formula II, III or IV:



(II)



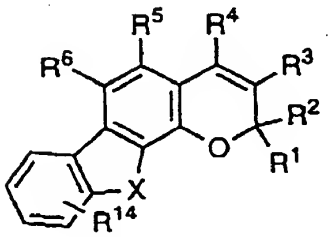
(III)



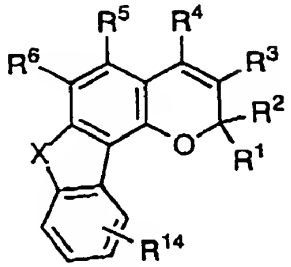
(IV)

wherein R^{14} and R^{15} are as defined for R^3, R^4, R^6- R^{10}.

6. A naphtho[1,2-*b*]pyran according to claim 5 of general formula V or VI:



(V)



(VI)

wherein X is selected from O, S, SO, SO_2, Se, NH, N-linear or branched C_1-C_{10} alkyl, N-aryl, N-heteroaryl, N-linear or branched C_1-C_{10} haloalkyl, N-linear or branched C_1-C_{10} perhaloalkyl, N-linear or branched C_1-C_{10}

hydroxyalkyl, N-linear or branched C_1-C_{10} alkoxyalkyl, benzyl, substituted benzyl, tosyl.

7. A naphtho[1,2-*b*]pyran according to any preceding claim, wherein R^1 is 4-morpholinophenyl, 4-piperidinophenyl, 4-dimethylaminophenyl or 4-pyrrolidinophenyl and R^5 is methoxycarbonyl.

8. A naphtho[1,2-*b*]pyran according to any of claims 1 to 6, wherein R^1 and R^2 are each 4-pyrrolidinophenyl and R^5 is methoxycarbonyl.

9. A naphtho[1,2-*b*]pyran according to any of claims 1 to 6, wherein R^1 is 4-morpholinophenyl, R^2 is 4-methoxyphenyl and R^5 is methoxycarbonyl.

10. A naphtho[1,2-*b*]pyran according to any of claims 1 to 6 wherein R^1 is 4-morpholinophenyl, R^2 is 2-thienyl and R^5 is methoxycarbonyl.

11. A polymeric host material including a naphtho[1,2-*b*]pyran according to any preceding claim.

12. A polymeric host material according to claim 11, wherein the material is a plastic or a glass.

13. A window, an optical filter, an ophthalmic lens or a sunglass lens made from a polymeric host material according to claim 11 or 12.

INTERNATIONAL SEARCH REPORT

Interna...nal Application No
PCT/GB 98/00905

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C07D311/92 C07D311/78 C07D409/04 G02B5/23

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C07D G02B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 95 16215 A (PPG INDUSTRIES INC) 15 June 1995 see the whole document see in particular examples page 12 ---	1-13
Y	EP 0 250 193 A (PLESSEY CO PLC) 23 December 1987 cited in the application see the whole document see in particular example 9 ---	1-13
Y	WO 96 04576 A (PPG INDUSTRIES INC) 15 February 1996 see the whole document --- -/--	5,7-13

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
24 June 1998	17.07.98

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Steendijk, M

2

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

Intern...onal Application No
PCT/GB 98/00905

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5 552 091 A (KUMAR ANIL) 3 September 1996 see the whole document see in particular examples column 11 ---	6-13
P,X	WO 98 04937 A (CHAN YOU PING ;BRYSON NATHAN (US); CORNING INC (US)) 5 February 1998 see the whole document ---	1-4,7-13
P,X	US 5 658 500 A (KUMAR ANIL ET AL) 19 August 1997 see the whole document see in particular examples column 11 -----	1-4,7-13

2

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/GB 98/00905

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9516215 A	15-06-1995	US 5458814 A	17-10-1995
		AU 1265895 A	27-06-1995
		US 5573712 A	12-11-1996
		US 5650098 A	22-07-1997
		US 5651923 A	29-07-1997
EP 0250193 A	23-12-1987	AU 598273 B	21-06-1990
		AU 7441687 A	24-12-1987
		BR 8703053 A	08-03-1988
		CA 1306643 A	25-08-1992
		DE 3787932 D	02-12-1993
		DE 3787932 T	24-02-1994
		GB 2193005 A	27-01-1988
		IN 170758 A	16-05-1992
		JP 63047721 A	29-02-1988
		US 4818096 A	04-04-1989
		ZA 8704317 A	17-12-1987
WO 9604576 A	15-02-1996	US 5514817 A	07-05-1996
		AU 683181 B	30-10-1997
		AU 3211795 A	04-03-1996
		EP 0801750 A	22-10-1997
		JP 10503212 T	24-03-1998
US 5552091 A	03-09-1996	US 5429774 A	04-07-1995
		WO 9420869 A	15-09-1994
		US 5411679 A	02-05-1995
WO 9804937 A	05-02-1998	FR 2751648 A	30-01-1998
		AU 3827097 A	20-02-1998
US 5658500 A	19-08-1997	NONE	